Molybdenum-Catalyzed Enantioselective Synthesis of Planar-Chiral (η^5-Phosphacyclopentadienyl)manganese(I) Complexes and Application in Asymmetric Catalysis

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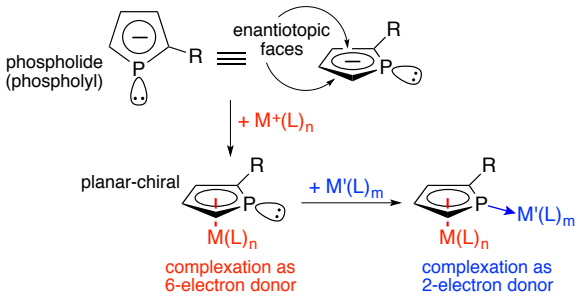
Supporting Information Placeholder

ABSTRACT: Enantioselective desymmetrization of C_s-symmetric (η^5-2,5-dialkenylphospholyl)(allyldiphenylphosphine)manganese(I) dicarbonyl complexes **1** was realized by the molybdenum-catalyzed asymmetric ring-closing metathesis (ARCM), and the corresponding bridged planar-chiral phosphacymantrene derivatives **2** were obtained in good yields with excellent enantioselectivity. The enantioselectivity of the ARCM reaction was strongly influenced by the structures of the phospholyl-bound alkenyl groups, and the highest enantioselectivity of up to 99% ee was achieved in the reaction of **1d** and **1e**, which possess the 2-methylpropenyl substituents at the 2- and 5-positions of the η^5-phospholides. Single-enantiomeric planar-chiral **2d**, which was obtained by the recrystallization of the highly enantiomerically enriched ARCM product, can serve as a chiral ligand for the palladium-catalyzed asymmetric allylic alkylation to show good enantioselectivity in up to 74 % ee.

INTRODUCTION

Phospholides (phospholyl anions; phosphacyclopentadienyl anions) are unique ligands in organometallic chemistry,[1] which primarily coordinate to a transition-metal cation in an η^5-fashion as six-electron donors to form the corresponding phosphametallocenes.[2] Whereas the phosphorus atom in a phosphametallocene still possesses a lone-pair on it, a phosphametallocene is capable of ligating to a second transition-metal as a phosphine-like two-electron donor. Unsymmetrical introduction of proper substituents onto a phospholide core makes the two faces of a planar phospholyl anion enantiotopic to each other. And thus, the η^5-coordination of an unsymmetric phospholide to a metal cation, which discriminates the two enantiotopic faces, induces "planar chirality" in the phosphametallocene species (Scheme 1).[3]

Scheme 1. Coordination Chemistry of Phospholides



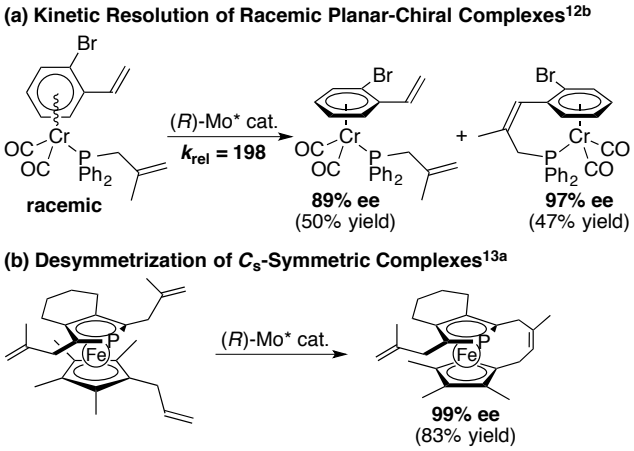
Since the initial discovery of phosphacymantrenes[4]/phosphaferrocenes[5] in the late 1970s, various planar-chiral phosphametallocenes have been prepared.[6] However, they were obtained in racemic forms and the enantiomeric resolution was not reported until the Ganter's first achievement in 1997.[7] Since then, various planar-chiral and "single-enantiomeric" phosphaferrocenes have been prepared and utilized as useful chiral ligands in metal-catalyzed asymmetric reactions.[3] Up until now, all the studies on the planar-chiral and scalemic phosphametallocenes are about iron(II) species (phosphaferrocenes), and the investigations on planar-chiral phosphacymantrenes have been virtually unexplored. It should be mentioned that the most optically active planar-chiral phosphaferrocenes were obtained by any one of the following; the enantiomeric resolution of the preformed racemates, the derivatization of the resolved precursors, or the diastereoselective separation utilizing chiral side-arms on the phosphaferrocene cores.

In the last few decades, we have been interested in modulating transition-metal complexes by the ring-closing metathesis (RCM) reaction.[8-10] The RCM strategies have been successfully extended to the enantioselective counterparts by using the Schrock-Hoveyda chiral molybdenum-alkylidene catalysts,[11] and various planar-chiral transition metal complexes have been prepared in excellent enantioselectivity either by the kinetic resolution of the racemic substrates[12] or by the desymmetrization of the C_s-symmetric precursors[13] (Scheme 2). These are the examples of catalytic asymmetric synthesis of planar-chiral transition-metal complexes, which is a research area rapidly developing recently.[14,15] The asymmetric ring-closing metathesis (ARCM) protocol was applicable to the desymmetrization of prochiral phosphaferrocenes and the corre-

sponding planar-chiral species were obtained in up to 99% ee (Scheme 2, (b)).[13a]

In this article, we would like to report the *catalytic* asymmetric synthesis of planar-chiral phosphacymantrene derivatives by the ARCM method. The C_s-symmetric substrate (see Figure 1) for this study possess an allylphosphine ligand and an η^5-2,5-bis(alkenyl)phospholide, where the two alkenyl substituents in the phospholide are identical and enantiotopic to each other. The molybdenum-catalyzed ARCM reaction between the two ligands takes place smoothly to desymmetrize the prochiral substrates, and the bridged planar-chiral products are obtained in high yields with excellent enantioselectivity of up to 99% ee. The simple recrystallization of the enantiomerically enriched planar-chiral ARCM product provided the enantiomerically pure phosphacymantrene species, which was applied to the palladium-catalyzed asymmetric allylic alkylation (the asymmetric Tsuji-Trost reaction)[16] as a chiral ligand to show the good enantioselectivity in up to 74% ee. It should be noted that, to the best of our knowledge, this work is the first example of preparing planar-chiral phosphacymantrenes in optically active forms.

Scheme 2. Enantioselective Synthesis of Planar-Chiral Transition-Metal Complexes by Asymmetric Ring-Closing Metathesis



RESULTS AND DISCUSSION

Design and Preparation of C_s-Symmetric (η^5-Phospholyl)manganese Substrates 1 for ARCM Desymmetrization. The substrates used in this study are (η^5-2,5-dialkenylphospholyl)(allyldiphenylphosphine)manganese(I) dicarbonyl (**1**), where the two alkenyl substituents at the 2- and 5-positions of the η^5-phospholyl ligand are identical. While the allyl group in the coordinating phosphine is a monosubstituted olefin, the two alkenyl groups in the η^5-phospholyl ligand are polysubstituted ones except for those in **1b**, which was designed and prepared for the control experiment (Figure 1).

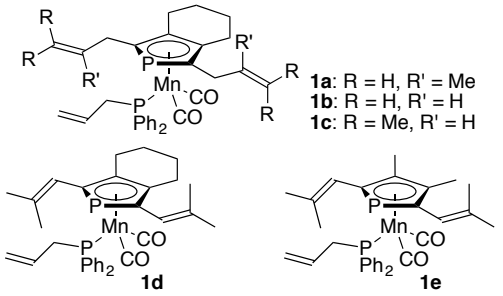
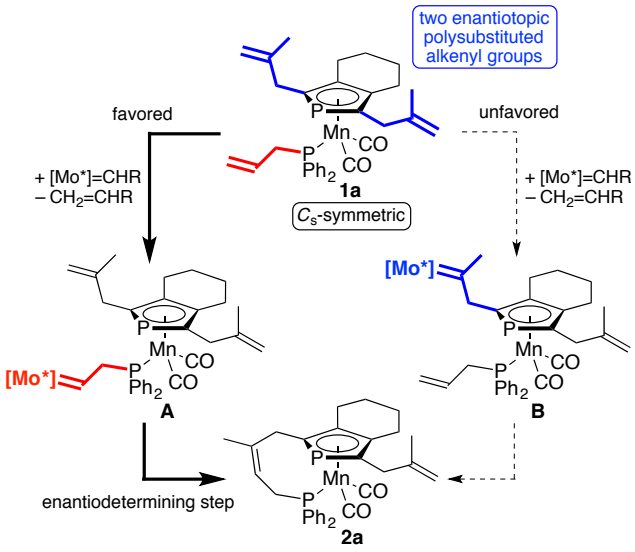


Figure 1. Structures of C_s-symmetric (η^5-phospholyl)manganese substrates **1a-e**.

The design concept of the substrates is explained in Scheme 3 for the ARCM reaction of **1a**. In general, less substituted olefins are more reactive than more substituted ones in olefin metathesis. And thus, the reaction pathway would be effectively regulated in the ARCM reaction of **1a** as explained below. The first step in the ARCM reaction between a chiral molybdenum-alkylidene precatalyst and **1a** might take place at the least substituted olefin in **1a**, that is the phosphorus-bound allyl group, to form intermediate **A**. Subsequently, the ring-closure in **A** proceeds intramolecularly to provide bridged product **2a**. The enantioselectivity of the ARCM process is determined in the second step, and the intramolecular nature of this step would effectively discriminate the two diastereotopic (*not* enantiotopic with the stereogenic Mo* moiety) phospholyl-bound alkenyl groups in **A** leading to the higher enantioselectivity in the ARCM reaction. Another possible reaction pathway is via intermediate **B**, and the enantiodetermining step in the latter pathway is the formation of **B**. Whereas the reaction between the chiral molybdenum-alkylidene species and **1a** giving **B** is an intermolecular process, the lesser enantiocontrol is presumed by this route. Consequently, the exclusion of the reaction pathway via **B** might be crucial for achieving high enantioselectivity in the present ARCM reaction. With the phospholyl-bound polysubstituted alkenyl groups in **1a,c-e**, the formation of intermediate **B** is less likely in the ARCM of **1a,c-e**. However, the two reaction pathways may compete in the ARCM of **1b**, and thus the lesser enantioselectivity is expected for the reaction.

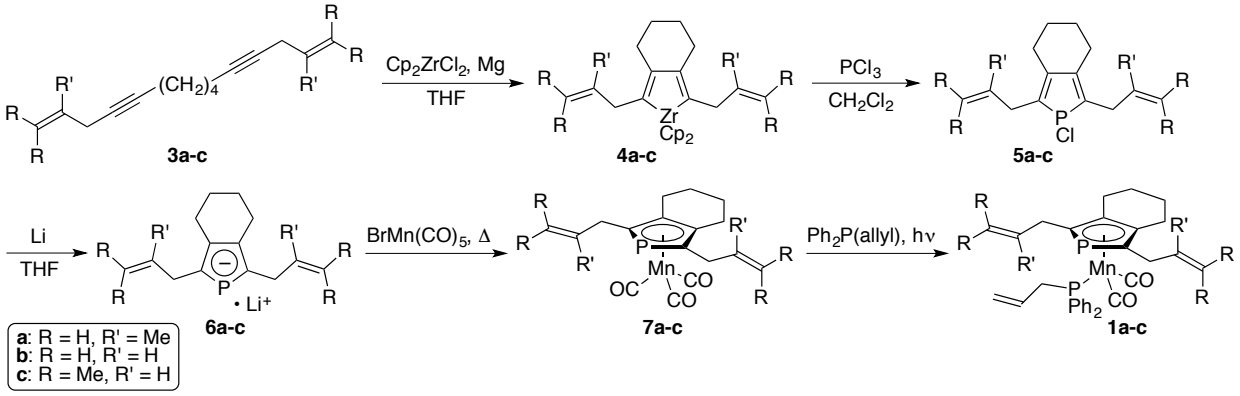
Scheme 3. Presumed ARCM Reaction Pathways from 1a to 2a



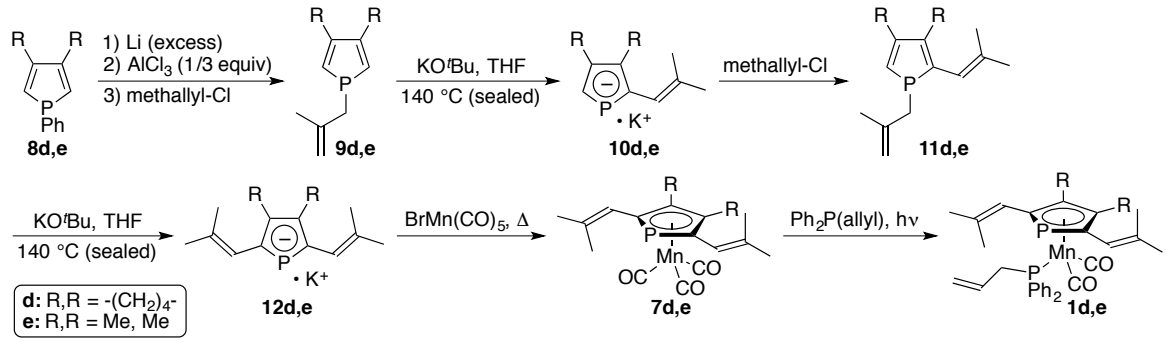
C_s-symmetric substrates **1a-c**, which have the allylic substituents at the 2- and 5-positions of the η^5-phospholide ligands, were prepared as outlined in Scheme 4. The conversion of **3** to **7** was carried out without isolating reactive synthetic intermediates **4-6** (see Experimental Section for detail). Treatment of 1,13-dien-4,10-diyne **3** with Cp_2ZrCl_2 in the presence of activated magnesium generated zirconacyclopentadiene **4**. The metallacycle transfer reaction of **4** with phosphorus trichloride afforded *P*-chlorophosphole **5**.[17] Subsequently, the reaction with lithium metal provided lithium phospholide **6** in situ, which was reacted with $BrMn(CO)_5$ to give phosphacymantrene **7** as a yellow oil. The photo-induced carbonyl-phosphine exchange reaction furnished **1** as a yellow crystalline solid.

On the other hand, substrates **1d,e** were prepared by a different method (Scheme 5). The 2-methylpropenyl substituents were introduced at the α-positions of the phospholide cores in **10** and **12** by the thermal [1,5]sigmatropic shift of the phosphorus-bound methallyl substituents in **9**/**11**,[18] which took place with a methallyl-to-(2-methylpropenyl) rearrangement. Subsequently, 2,5-bis(2-methylpropenyl)phospholides **12d,e** thus obtained were converted to the corresponding phosphacymantrene derivatives **7** and **1** by the standard methods. In the synthetic sequence shown in Scheme 5, reactive intermediates **9-12** were not isolated, and the reaction progress was monitored by the ^{31}P-NMR in the protio-solvents (i.e., the reaction solvents. See Experimental Section for detail). It should be noted that phospholides having vinylic substituents at the 2- and 5-positions (such as **12d,e**) could not be prepared by the zirconacycle-mediated method as in Scheme 4. The reactions between Cp_2ZrCl_2/Mg and 1,11-dien-3,9-diynes gave complex mixtures and the desired 2,5-divinylzirconacyclopentadienes could not be obtained because the conjugated enyne moieties in 1,11-dien-3,9-diynes might react with the Zr(II) species in the different manners.[19]

Scheme 4. Preparation of C_s-Symmetric Phosphacymantrene Substrates 1a-c



Scheme 5. Preparation of C_s-Symmetric Phosphacymantrene Substrates 1d,e



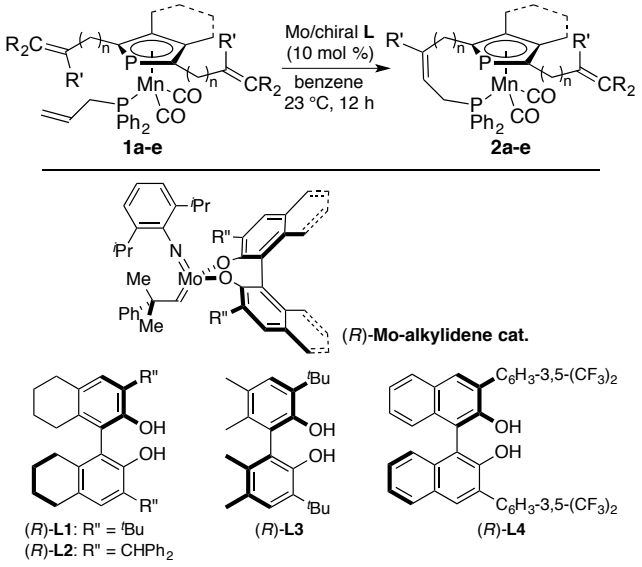
Enantioselective Desymmetrization of C_s-Symmetric 1 by Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis (ARCM). The prepared substrates were subjected to the desymmetrization studies with various chiral molybdenum-alkylidene precatalysts, and the results are summarized in Table 1. Screening of the chiral precatalysts was examined using **1a** as a prototypical substrate. The reactions were carried out in benzene at 23 °C in the presence of an appropriate chiral molybdenum-alkylidene precatalyst (10 mol %), that was generated in situ from the molybdenum precursor, (pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=N-C$_6$H$_3$-2,6-*i*Pr$_2$), and an axially chiral biphenol derivative.[20] Under these conditions, the Mo-precatalyst generated with (*R*)-**L1**[21a] showed insufficient catalytic activity with poor enantioselectivity giving RCM product (−)-**2a** in 87% conversion and 31% ee (Table 1, entry 1). The molybdenum precatalyst coordinated with (*R*)-**L2**[21b] showed complete conversion of **1a** under otherwise identical conditions with excellent enantioselectivity giving (−)-**2a** in 91% ee (entry 2). On the other hand, Mo/(*R*)-**L3**,[21c] which was the best catalyst in the kinetic resolution of planar-chiral bromocymantrene derivatives,[12e] was inappropriate for the desymmetrization reaction affording (−)-**2a** in 98% conversion with 61% ee (entry 3). The Mo precatalyst prepared with (*R*)-**L4**,[21d] which was the most effective catalyst in the desymmetrization of C_s-symmetric phosphaferrocenes,[13a] also showed reasonable performance; (−)-**2a** was obtained quantitatively in 72% ee (entry 4).

After the optimization studies, Mo/(*R*)-**L2** and/or Mo/(*R*)-**L4** were applied to the other substrates. Substrate **1b** possesses the two

enantiotopic phospholyl-bound allyl substituents in place of the methallyl groups in **1a**. Because all the three alkenyl substituents in **1b** are monosubstituted olefins, the discrimination between the phospholyl-bound allyl groups and the allyl substituent of the phosphine ligand was not effective in the ARCM of **1b**. As we expected, indeed, the desymmetrization reaction of **1b** by Mo/(*R*)-**L2** was poorly enantioselective and provided nearly racemic **2b** of less than 1% ee (entry 5). The results in entries 2 and 5 support the validity of the reaction pathways discussed in Scheme 3 (see above). It was found that the phospholyl-bound prenyl groups effectively differentiated the reactivity among the alkenyl substituents in **1c** leading to the reasonable enantioselectivity in its ARCM reaction (entries 6 and 7). While cyclized product (–)-**2c** was obtained in 58% ee quantitatively using Mo/(*R*)-**L2**, the reaction by Mo/(*R*)-**L4** gave (–)-**2c** in 89% ee. However, the trisubstituted olefin moiety in the prenyl groups somewhat reduced the reactivity of **1c** toward the ring-closure, and the conversion of the reaction using Mo/(*R*)-**L4** remained in only 27% (entry 7).

Meanwhile, the substrates with the 2-methylpropenyl (β,β-dimethylvinyl) groups on the phospholide core showed far better enantioselectivity in the present desymmetrization reaction. The ARCM reaction of **1d** catalyzed by Mo/(*R*)-**L2** proceeded smoothly and the corresponding bridged product (–)-**2d** was obtained in 97% ee and >99% yield (entry 8). In the same way, the ARCM reaction of **1e** provided (–)-**2e** in >99% yield and in 99% ee in the presence of Mo/(*R*)-**L2** (entry 10). The molybdenum-alkylidene precatalyst coordinated with (*R*)-**L4** was not effective for the reactions of **1d** and **1e** affording the ARCM products of low enantioselectivity ranging from 14 to 17 % ee (entries 9 and 11).

Table 1. Molybdenum-Catalyzed ARCM Desymmetrization of C_s-Symmetric Phosphacymantrene 1a-e[a]



entry	substrate	chiral **L**	conversion (%)[b]	%ee[c,d]
1	**1a**	(*R*)-**L1**	87	31 (–)
2	**1a**	(*R*)-**L2**	>99 (>99)	91 (–)
3	**1a**	(*R*)-**L3**	98	61 (–)
4	**1a**	(*R*)-**L4**	>99	72 (–)
5	**1b**	(*R*)-**L2**	>99 (77)	<1 (n.d.)
6	**1c**	(*R*)-**L2**	>99 (>99)	58 (–)
7	**1c**	(*R*)-**L4**	27	89 (–)
8	**1d**	(*R*)-**L2**	>99 (>99)	97 (*R*)
9	**1d**	(*R*)-**L4**	98	14 (*R*)
10	**1e**	(*R*)-**L2**	>99 (>99)	99 (–)
11	**1e**	(*R*)-**L4**	98	17 (–)

[a] The reaction was carried out using **1** (35 μmol) in benzene for 12 h in the presence of an appropriate molybdenum-alkylidene precatalyst that was generated in situ (10 mol %) unless otherwise noted. [b] Determined by the ^{31}P-NMR analysis. The numbers in parentheses are the isolated yields after purification by silica gel column chromatography. [c] Determined by HPLC on a chiral stationary phase (see Experimental Section for details). [d] Sign of specific rotation or absolute configuration of the products in parentheses.

Determination of Absolute Configuration of (–)-2d. Single crystals of the levorotatory enantiomer of **2d** ($[\alpha]_D^{24}$ = –91.3 (*c* = 2.60, EtOAc) for the sample of 97% ee) suitable for X-ray crystallography were grown from a cold pentane solution as orange prisms. The crystal structure of (–)-**2d**, which is with disorder at the phospholyl-bound tetramethylene moiety, is shown in Figure 2 with the selected bond lengths and angles.[22] The Flack parameter was determined to be 0.03(2) for the structure, and the absolute configuration of (–)-**2d** is unambiguously assigned to be (*R*) (see Supporting Information for details). The configurations of the other desymmetrization products were deduced by analogy.

The distance between Mn1 and the η^5-phospholyl centroid is 1.777(4) Å, which is comparable to those in the analogous bridged cymantrene derivatives.[9g,h] The crystal structure shows the distortion in **2d** from the ideal three-legged piano-stool structure due to the short C_3-bridge between the η^5-phospholyl and the Mn1-bound phosphine; while C(carbonyl)-Mn1-phospholyl centroid angles are 124.67(8) and 124.58(8), P2-Mn1-phospholyl centroid angle is considerably smaller (120.12(9)°).

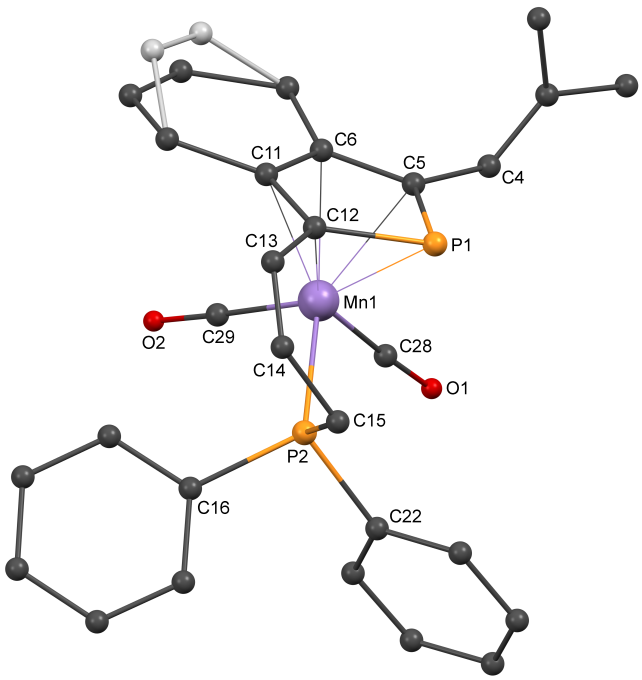
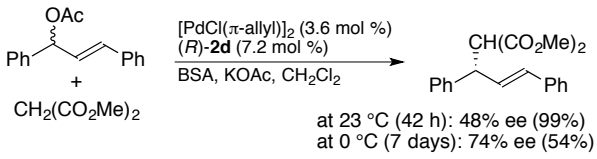


Figure 2. Ball-and-stick drawing of (*R*)-(–)-**2d** with selected atom numbering. Selected bond lengths (Å) and angles (deg): P1-C5 =

1.786(3), P1-C12 = 1.803(3), C5-C6 = 1.415(4), C6-C11 = 1.427(4), C11-C12 = 1.401(4), Mn1-P1 = 2.3720(9), Mn1-P2 = 2.2432(8), Mn1-C5 = 2.170(3), Mn1-C6 = 2.174(3), Mn1-C11 = 2.196(3), Mn1-C12 = 2.183(3), Mn1-Phospholyl Centroid = 1.778(4); C5-P1-C12 = 89.0(1), P2-Mn1-Phospholyl Centroid = 120.12(9), C28-Mn1-Phospholyl Centroid = 124.67(8), C29-Mn1-Phospholyl Centroid = 124.58(8).

Application of Planar-Chiral (*R*)-(–)-2d to Palladium-Catalyzed Asymmetric Allylic Alkylation. Recrystallization of (*R*)-**2d** (97% ee), which was obtained as in Table 1 (entry 8), provided enantiomerically pure (*R*)-**2d**. Potential usefulness of the planar-chiral bridged phosphacymantrene derivative was explored for the palladium-catalyzed asymmetric allylic alkylation reaction.[16] The palladium complexes generated in situ from $[PdCl(\pi\text{-allyl})]_2$ and (*R*)-**2d** (Pd/(*R*)-**2d** = 1/1) catalyzed the reaction of racemic 1,3-diphenyl-2-propenyl acetate with dimethyl malonate in the presence of BSA to give the alkylation product in 48% ee and in 99% yield at 23 °C. The enantioselectivity could be improved to 74% ee at 0 °C, but the reaction was slow at this temperature (Scheme 6). Although these results need further improvement, the reaction shown in Scheme 6 clearly indicates the potential validity of planar-chiral phosphacymantrene derivatives in asymmetric synthesis. To the best of our knowledge, this is the first example of utilizing a planar-chiral phosphacymantrene as a chiral ligand in transition-metal catalysis.

Scheme 6. Pd-Catalyzed Asymmetric Allylic Alkylation of *rac*-1,3-Diphenyl-2-propenyl Acetate



CONCLUSIONS

In summary, we have developed a highly efficient method for the enantioselective desymmetrization of C_s-symmetric (η^5-2,5-dialkenylphospholyl)(allyldiphenylphosphine)manganese(I) dicarbonyl complexes **1** by the molybdenum-catalyzed asymmetric ring-closing metathesis (ARCM). Various bridged planar-chiral phosphacymantrene derivatives **2** were prepared in near-quantitative yields with excellent enantioselectivity of up to 99% ee by this method. It was observed that the enantioselectivity of the ARCM reaction was strongly influenced by the structure of the phospholyl-bound alkenyl groups, and the highest enantioselectivity of 97-99% ee was achieved in the reaction of **1d** and **1e**, which possess the 2-methylpropenyl substituents at the 2-, and 5-positions of the η^5-phospholides. Recrystallization of the highly enantiomerically enriched ARCM product, **2d** of 97% ee, gave enantiomerically pure **2d**, which could serve as a chiral ligand for the palladium-catalyzed asymmetric allylic alkylation to show good enantioselectivity in up to 74 % ee.

EXPERIMENTAL SECTION

General Information. All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 100 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR (at 162 MHz) chemical shifts are externally referenced to 85% H_3PO_4. Tetrahydrofuran and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. 2,13-Dimethyltetradeca-1,13-dien-4,10-diyne (**3a**),[13a] tetradeca-1,13-dien-4,10-diyne (**3b**),[9b] 1,2-dimethylenecyclohexane,[23] 3,4-dimethyl-1-phenylphosphole (**8e**),[24] (pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=N-C$_6$H$_3$-2,6-^{i}Pr$_2$),[18] (*R*)-3,3'-^{t}Bu$_2$-H$_8$-binaphthol (**L1**),[21a] (*R*)-3,3'-(Ph$_2$CH)$_2$-H$_8$-binaphthol (**L2**),[21b] (*R*)-3,3'-[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$-2,2'-binaphthol (**L4**)[21d] were prepared according to the reported methods. All the other chemicals were obtained from commercial sources and used as received unless otherwise noted.

2,15-Dimethylhexadeca-2,14-dien-5,11-diyne (3c). To a solution of ^{n}PrMgBr, prepared from ^{n}PrBr (23.5 g, 191 mmol) and Mg (4.59 g, 189 mmol) in THF (160 mL), was added 1,7-octadiyne (8.73 g, 82.2 mmol) dropwise by means of syringe at 0 °C. After stirring the mixture for 3 h at room temperature, to this were added CuCl (3.3 g, 33 mmol) and 4-chloro-2-methyl-2-butene (23.3 g, 222 mmol) successively, then the mixture was stirred at 60 °C for 3 h. The reaction mixture was quenched with saturated NH_4Cl, then partitioned between hexane and H_2O. The hexane layer was washed with brine, dried over $MgSO_4$, filtered, then evaporated. The GC and NMR analyses of the crude mixture showed the presence of ca. 5% of 3,3,14-trimethylpentadeca-1,13-dien-4,10-diyne, which could be removed by careful vacuum-distillation. Colorless oil. Yield: 8.38 g (34%). ^{1}H NMR ($CDCl_3$): δ 1.57 (m, 4H), 1.62 (s, 6H), 1.70 (s, 6H), 2.17 (t, *J* = 2.4 Hz, 4H), 2.85 (d, *J* = 6.8 Hz, 4H), 5.18 (tt, *J* = 7.2 and 1.6 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.6, 17.9, 18.4, 25.5, 28.2, 79.1, 79.4, 119.9, 133.2. EI-HRMS Calcd for $C_{18}H_{26}$: 242.2035. Found: 242.2025.

Preparation of (η^5-Phospholyl)Mn(I)(CO)$_3$ Derivatives (7a-c). A typical procedure is given for the synthesis of **7a**. To a suspension of Mg (251 mg, 10.3 mmol) in THF (1 mL), which was activated with 1,2-dibromoethane (22 μL, 0.26 mmol), was added a solution of **3a** (2.19 g, 10.2 mmol) and Cp_2ZrCl_2 (2.94 g, 10.1 mmol) in THF (30 mL) via cannula at room temperature, and the mixture was stirred overnight. The mixture was evaporated to dryness under reduced pressure and the residue was partially dissolved in CH_2Cl_2 (50 ml). To the resulting suspension was added phosphorus trichloride (1.8 mL, 21 mmol) at 0 °C, and the mixture was stirred at room temperature for 3 h. All the volatiles were removed under reduced pressure, then the residue was extracted with hexane (30 mL × 3) and the combined hexane extract was filtrated through dried Celite. After removing the solvent under reduced pressure, *P*-chlorophosphole **5a** thus obtained was treated with excess lithium wire (ca. 500 mg, ca. 72 mmol) in THF (20 mL) to give a solution of lithium phospholide **6a**. In a different flask, $BrMn(CO)_5$ (2.50 g, 9.10 mmol) was taken, and to this was added the solution of **6a** obtained as above at room temperature. The resulting mixture was stirred at room temperature for 12 h. The mixture was evaporated to dryness under reduced pressure, then the residue was dissolved in xylenes (15 mL). The mixture was heated to 120 °C and stirred for 12 h. After cooling to room temperature, the mixture was filtered through a pad of Celite, and the filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel (hexane/benzene = 10/1) under nitrogen to give **7a** as a yellow oil. The reaction conditions were not optimized. The characterization data for **7a-c** are given below.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-dimethallylphospholyl]manganese(I) Tricarbonyl (7a). Yellow oil. Yield: 1.19 g (34%) from $BrMn(CO)_5$ (2.50 g, 9.10 mmol). ^1H NMR (C_6D_6): δ 1.25-1.31 (m, 2H), 1.54 (s, 6H), 1.57-1.66 (m, 2H), 2.08-2.23 (m, 4H), 2.54 (d, J = 11.0 Hz, 4H), 4.61 (br, 2H), 4.71 (br, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.4 (s), 22.6 (d, J_{PC} = 2.8 Hz), 24.1 (s), 36.4 (d, J_{PC} = 17.9 Hz), 110.9 (d, J_{PC} = 60.9 Hz), 112.1 (d, J_{PC} = 1.6 Hz), 113.9 (d, J_{PC} = 5.7 Hz), 144.2 (d, J_{PC} = 1.3 Hz), 225.2 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ –23.1 (s). Anal. Calcd for $C_{19}H_{22}MnO_3P$: C, 59.38; H, 5.77. Found: C, 59.39; H, 5.79. EI-HRMS Calcd for $C_{19}H_{22}MnO_3P$: 384.0687. Found: 384.0674.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-diallylphospholyl]manganese(I) Tricarbonyl (7b). Yellow oil. Yield: 769 mg (29%) from $BrMn(CO)_5$ (2.05 g, 7.42 mmol). ^1H NMR (C_6D_6): δ 1.22-1.33 (m, 2H), 1.56-1.64 (m, 2H), 1.92-2.02 (m, 2H), 2.11-2.20 (m, 2H), 2.48-2.56 (m, 4H), 4.85-4.94 (m, 4H), 5.56-5.68 (m, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.4 (s), 24.2 (s), 32.9 (d, J_{PC} = 17.7 Hz), 111.9 (d, J_{PC} = 60.6 Hz), 113.4 (d, J_{PC} = 5.9 Hz), 116.6 (s), 136.5 (d, J_{PC} = 4.9 Hz), 225.2 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ –34.0 (s). EI-HRMS Calcd for $C_{17}H_{19}MnO_3P$ (M+1): 357.0452. Found: 357.0440.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-diprenylphospholyl]manganese(I) Tricarbonyl (7c). Yellow oil. Yield: 730 mg (19%) from $BrMn(CO)_5$ (2.54 g, 9.24 mmol). ^1H NMR (C_6D_6): δ 1.27-1.32 (m, 2H), 1.50 (s, 6H), 1.59 (s, 6H), 1.62-1.67 (m, 2H), 1.98 -2.05 (m, 2H), 2.31-2.25 (m, 2H), 2.64 (m, 4H), 5.20 (t, J = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 17.9 (s), 22.5 (s), 24.4 (s), 25.6 (s), 27.5 (d, J_{PC} = 17.4 Hz), 113.2 (d, J_{PC} = 5.5 Hz), 113.8 (d, J_{PC} = 49.7 Hz), 123.0 (d, J_{PC} = 5.3 Hz), 133.5 (s), 225.6 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ –25.6 (s). EI-HRMS Calcd for $C_{21}H_{27}MnO_3P$ (M+1): 413.1078. Found: 413.1084.

3,4-(Butane-1,4-diyl)-1-phenylphosphole (8d). This compound was prepared by the method reported by Mathey, et al.[24] A mixture of dichlorophenylphosphine (7.56 g, 42.2 mmol) and 1,2-dimethylenecyclohexane (ca. 80% purity, 9.14 g, ca. 67.7 mmol) was place in a flask under nitrogen, and kept stirred for 10 days at room temperature to give a white solid. Remaining 1,2-dimethylenecyclohexane was removed under vacuum, and the remaining solid was suspended in a mixture of hexane (30 mL) and dichloromethane (15 mL). To this was added 2-methylpyridine (8.76 mL, 88.7 mmol) in dichloromethane (15 mL) dropwise, and the mixture was stirred for 12 h. The solution was hydrolyzed with 3N HCl (ca. 20 mL). The organic layer was separated, washed with water and brine, and dried over $MgSO_4$. The crude compound was purified by silica gel chromatography (hexane/benzene = 1/1) under nitrogen to give the title compound as a colorless semi-solid. Yield: 4.75 g (53%). ^1H NMR ($CDCl_3$): δ 1.85 (br, 4H), 2.82 (br, 4H), 6.62 (m, J = 38.6 Hz, 2H), 7.38-7.41 (m, 3H), 7.48-7.53 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.7 (s), 29.0 (d, J_{PC} = 3.8 Hz), 127.6 (s), 128.3 (d, J_{PC} = 7.7 Hz), 128.6 (s), 132.2 (d, J_{PC} = 12.0 Hz), 133.1 (d, J_{PC} = 18.2 Hz), 149.2 (d, J_{PC} = 8.2 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.8. Anal. Calcd for $C_{14}H_{15}P$: C, 78.49; H, 7.06. Found: C, 78.68; H, 7.06. EI-HRMS Calcd for $C_{14}H_{15}P$: 214.0911. Found: 214.0906.

Preparation of (η⁵-Phospholyl)Mn(I)(CO)₃ Derivatives (7d,e). A typical procedure is given for the synthesis of **7d**. A mixture of **8d** (3.70 g, 17.3 mg) and lithium wire (1.20 g, 173 mmol) in THF (25 mL) was stirred at room temperature for 12 h. Remaining excess lithium metal was removed by filtration, then $AlCl_3$ (768 mg, 5.76 mmol) was added to the filtrate at 0 °C. After stirring the solution at room temperature for 1 h, methallyl chloride (3.15 g, 34.7 mmol) was added at 0 °C. All the volatiles were removed under reduced pressure, and the residue was dissolved in benzene, which was then passed through a pad of silica gel to give crude **9d** (2.10 g, 10.9 mmol; ^{31}P NMR in benzene: δ –4.3). A mixture of crude **9d** (2.10 g) and ^{t}BuOK (1.47 g, 13.1 mmol) in THF (20 mL) was heated in a sealed tube for 3 h at 140 °C. Resulting phospholide **10d** (^{31}P NMR in THF: δ 77.3) was then treated with methallyl chloride (3.03 g, 33.5 mmol). The reaction mixture was roughly purified by short silica gel column eluting with benzene to give crude **11d** (2.01 g, 8.16 mmol; ^{31}P NMR in benzene: δ –1.8), which was then treated with ^{t}BuOK (1.10 g, 9.80 mmol) in THF (20 mL) in a sealed tube for 3 h at 140 °C. The THF solution of phospholide **12d** thus obtained (^{31}P NMR in THF: δ 82.6) was reacted with $BrMn(CO)_5$ (1.92 g, 6.98 mmol) at room temperature for 12 h. The mixture was evaporated to dryness under reduced pressure, then the residue was dissolved in xylenes (15 mL). The mixture was heated to 120 °C and stirred for 12 h. After cooling to room temperature, the mixture was filtered through a pad of Celite, and the filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel (hexane/benzene = 10/1) under nitrogen to give **7d** as a yellow solid. The reaction conditions were not optimized. The ^{31}P NMR data for the synthetic intermediates to **7e**: **9e**, δ –7.4 (benzene); **10e**, δ 72.4 (THF); **11e**, δ –14.7 (benzene); **12e**, δ 79.8 (THF). The characterization data for **7d,e** are given below.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-di(2-methylpropenyl)phospholyl]manganese(I) Tricarbonyl (7d). Yellow oil. Yield: 1.36 g (51%) from $BrMn(CO)_5$ (1.92 g, 6.98 mmol). ^1H NMR (C_6D_6): δ 1.27-1.33 (m, 2H), 1.59 (s, 6H), 1.65-1.72 (m, 2H), 1.86 (s, 6H), 2.06-2.13 (m, 2H), 2.33-2.41 (m, 2H), 5.66 (br d, J = 12.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.8 (d, J_{PC} = 17.6 Hz), 22.6 (s), 25.1 (s), 27.1 (s), 109.4 (d, J_{PC} = 65.0 Hz), 111.9 (d, J_{PC} = 5.5 Hz), 118.5 (d, J_{PC} = 11.5 Hz), 138.7 (s), 225.5 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ –27.2. Anal. Calcd for $C_{19}H_{22}MnO_3P$: C, 59.38; H, 5.77. Found: C, 59.38; H, 5.71. EI-HRMS Calcd for $C_{19}H_{22}MnO_3P$: 384.0687. Found: 384.0676.

[η⁵-3,4-Dimethyl-2,5-di(2-methylpropenyl)phospholyl]manganese(I) Tricarbonyl (7e). Yellow oil. Yield: 1.49 g (41%) from $BrMn(CO)_5$ (2.80 g, 10.2 mmol). ^1H NMR (C_6D_6): δ 1.57 (s, 6H), 1.76 (s, 6H), 1.78 (s, 6H), 5.65 (br d, J = 10.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 13.2 (s), 20.5 (d, J_{PC} = 15.2 Hz), 26.8 (s), 108.8 (d, J_{PC} = 5.5 Hz), 113.4 (d, J_{PC} = 63.2 Hz), 118.8 (d, J_{PC} = 12.8 Hz), 139.5 (s), 225.2 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ –33.0. Anal. Calcd for $C_{17}H_{20}MnO_3P$: C, 56.94; H, 5.63. Found: C, 56.56; H, 5.57. EI-HRMS Calcd for $C_{17}H_{20}MnO_3P$: 358.0531. Found: 358.0527.

Preparation of (η⁵-Phospholyl)Mn(I)(CO)₂(phosphine) Derivatives (1a-e). A benzene solution (10 mL) of **7** (0.50 mmol) and allyldiphenylphosphine (0.50 mmol) was irradiated by mercury lamp (300 W, Eikosha Inc.) for 15 h at room temperature. The resulting solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc = 10/1) under nitrogen to give **1** as a yellow solid. The characterization data for **1a-e** are given below.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-dimethallylphospholyl](allyldiphenylphosphine)manganese(I) Dicarbonyl (1a). Yellow solid. Mp: 112.0-112.3 °C. Yield: 1.22 g (68%) from **7a** (1.18 g, 3.07 mmol). ^{1}H NMR ($CDCl_3$): δ 1.57 (s, 6H), 1.57-1.62 (m, 2H), 1.67-1.74 (m, 2H), 1.89-1.98 (m, 2H), 2.32-2.57 (m, 6H), 3.31 (t, *J* = 8.4 Hz, 2H), 4.47 (br, 2H), 4.63 (br, 2H), 4.77 (br d, *J* = 16.9 Hz, 1H), 4.90 (br d, *J* = 10.1 Hz, 1H), 5.46-5.58 (m, 1H), 7.33-7.40 (m, 6H), 7.56-7.60 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.5 (d, J_{PC} = 2.4 Hz), 22.7 (s), 24.0 (s), 35.1 (d, J_{PC} = 18.5 Hz), 42.6 (dd, J_{PC} = 26.8 and 4.7 Hz), 104.9 (d, J_{PC} = 57.1 Hz), 110.6 (s), 111.0 (dd, J_{PC} = 5.3 and 2.3 Hz), 119.1 (d, J_{PC} = 10.6 Hz), 127.9 (d, J_{PC} = 8.9 Hz), 129.3 (d, J_{PC} = 2.1 Hz), 130.7 (d, J_{PC} = 5.3 Hz), 132.7 (dd, J_{PC} = 8.9 and 1.8 Hz), 138.7 (d, J_{PC} = 39.2 Hz), 145.5 (s), 231.6 (d, J_{PC} = 26.2 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –11.6 (s), 84.2 (br). Anal. Calcd for $C_{33}H_{37}MnO_2P_2$: C, 68.04; H, 6.40. Found: C, 68.23; H, 6.49. EI-HRMS Calcd for $C_{33}H_{37}MnO_2P_2$: 582.1649. Found: 582.1641.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-diallylphospholyl](allyldiphenylphosphine)manganese(I) Dicarbonyl (1b). Yellow solid. Mp: 107.3-107.5 °C. Yield: 740 mg (63%) from **7b** (755 mg, 2.12 mmol). ^{1}H NMR ($CDCl_3$): δ 1.66-1.84 (m, 4H), 1.89-2.01 (m, 2H), 2.31-2.42 (m, 2H), 2.45-2.60 (m, 4H), 3.31 (t, *J* = 8.2 Hz, 2H), 4.71-4.93 (m, 6H), 5.44-5.64 (m, 3H), 7.32-7.41 (m, 6H), 7.53-7.61 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.6 (s), 24.1 (s), 31.5 (d, J_{PC} = 18.8 Hz), 42.6 (dd, J_{PC} = 26.6 and 4.3 Hz), 105.8 (d, J_{PC} = 57.1 Hz), 110.4 (d, J_{PC} = 3.5 Hz), 114.8 (s), 119.0 (d, J_{PC} = 10.4 Hz), 127.8 (d, J_{PC} = 8.9 Hz), 129.2 (s), 130.6 (d, J_{PC} = 5.1 Hz), 132.6 (d, J_{PC} = 8.6 Hz), 138.2 (d, J_{PC} = 2.6 Hz), 138.6 (d, J_{PC} = 38.8 Hz), 231.5 (d, J_{PC} = 26.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –16.5 (s), 83.8 (s). EI-HRMS Calcd for $C_{31}H_{34}MnO_2P_2$ (M+1): 555.1415. Found: 555.1409.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-diprenylphospholyl](allyldiphenylphosphine)manganese(I) Dicarbonyl (1c). Yellow solid. Mp: 119.1-119.4 °C. Yield: 650 mg (61%) from **7c** (720 mg, 1.75 mmol). ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 6H), 1.60 (s, 6H), 1.70-1.81 (m, 4H), 1.93-2.01 (m, 2H), 2.32-2.46 (m, 4H), 2.53-2.60 (m, 2H), 3.32 (t, *J* = 8.4 Hz, 2H), 4.75 (br d, *J* = 16.8 Hz, 1H), 4.87-4.93 (m, 3H), 5.51-5.59 (m, 1H), 7.34-7.40 (m, 6H), 7.56-7.61 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.9 (s), 22.6 (s), 24.2 (s), 25.6 (s), 26.2 (d, J_{PC} = 18.6 Hz), 42.9 (dd, J_{PC} = 26.4 and 4.4 Hz), 108.1 (d, J_{PC} = 56.9 Hz), 110.1 (d, J_{PC} = 3.3 Hz), 118.8 (d, J_{PC} = 10.3 Hz), 124.3 (d, J_{PC} = 3.5 Hz), 127.8 (d, J_{PC} = 8.9 Hz), 129.2 (d, J_{PC} = 1.3 Hz), 130.9 (d, J_{PC} = 5.3 Hz), 131.3 (s), 132.7 (d, J_{PC} = 8.8 Hz), 138.7 (d, J_{PC} = 38.4 Hz), 231.8 (d, J_{PC} = 26.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –17.8 (s), 83.8 (s). EI-HRMS Calcd for $C_{35}H_{42}MnO_2P_2$ (M+1): 611.2041. Found: 611.2013.

[η⁵-3,4-(Butan-1,4-diyl)-2,5-di(2-methylpropenyl)phospholyl](allyldiphenylphosphine)manganese(I) Dicarbonyl (1d). Yellow solid. Mp: 164.3-164.7 °C. Yield: 1.58 g (77%) from **7d** (1.35 g, 3.51 mmol). ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 12H), 1.75-1.78 (m, 2H), 1.98-2.04 (m, 2H), 2.34-2.41 (m, 2H), 2.68-2.75 (m, 2H), 3.22 (t, *J* = 8.4 Hz, 2H), 4.77 (dd, *J* = 17.2 and 2.4 Hz, 1H), 4.87 (d, *J* = 9.6 Hz, 1H), 5.35 (d, *J* = 12.4 Hz, 2H), 5.47-5.55 (m, 1H), 7.26-7.34 (m, 6H), 7.43-7.47 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.0 (d, J_{PC} = 20.0 Hz), 23.0 (s), 25.1 (s), 27.3 (s), 41.8 (dd, J_{PC} = 26.5 and 2.7 Hz), 103.5 (d, J_{PC} = 60.6 Hz), 108.9 (d, J_{PC} = 4.5 Hz), 119.0 (d, J_{PC} = 10.2 Hz), 119.4 (d, J_{PC} = 10.9 Hz), 127.6 (d, J_{PC} = 9.1 Hz), 128.9 (s), 131.1 (d, J_{PC} = 5.2 Hz), 132.6 (d, J_{PC} = 9.2 Hz), 135.8 (s), 138.2 (d, J_{PC} = 39.5 Hz), 231.7 (d, J_{PC} = 25.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –12.6 (s), 83.5 (s). Anal. Calcd for $C_{33}H_{37}MnO_2P_2$: C, 68.04; H, 6.40. Found: C, 67.86; H, 6.61. EI-HRMS Calcd for $C_{33}H_{37}MnO_2P_2$: 582.1649. Found: 582.1649.

[η⁵-3,4-Dimethyl-2,5-di(2-methylpropenyl)phospholyl](allyldiphenylphosphine)manganese(I) Dicarbonyl (1e). Yellow solid. Mp: 135.3-135.6 °C. Yield: 1.67 g (73%) from **7e** (1.48 g, 4.13 mmol). ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 6H), 1.61 (s, 6H), 2.10 (s, 6H), 3.21 (dd, *J* = 9.0 and 7.9 Hz, 2H), 4.75-4.81 (m, 1H), 4.86-4.90 (m, 1H), 5.32 (br d, 11.6 Hz, 2H), 5.47-5.59 (m, 1H), 7.26-7.35 (m, 6H), 7.43-7.49 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.8 (s), 19.9 (d, J_{PC} = 15.2 Hz), 27.3 (s), 41.7 (d, J_{PC} = 26.2 Hz), 105.8 (d, J_{PC} = 59.5 Hz), 106.7 (d, J_{PC} = 4.8 Hz), 119.1 (d, J_{PC} = 10.3 Hz), 119.8 (d, J_{PC} = 12.2 Hz), 127.7 (d, J_{PC} = 9.1 Hz), 129.1 (s), 131.1 (d, J_{PC} = 5.5 Hz), 132.7 (d, J_{PC} = 7.9 Hz), 136.4 (s), 138.1 (d, J_{PC} = 39.4 Hz), 231.9 (d, J_{PC} = 24.9 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –15.4 (s), 83.0 (s). Anal. Calcd for $C_{31}H_{35}MnO_2P_2$: C, 66.91; H, 6.34. Found: C, 66.86; H, 6.63. EI-HRMS Calcd for $C_{31}H_{35}MnO_2P_2$: 556.1493. Found: 556.1477.

General Procedure for Molybdenum-Catalyzed ARCM Desymmetrization of 1. In a glovebox, Mo(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(=CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ (1.9 mg, 3.5 μmol) and an appropriate chiral ligand **L** (3.6 μmol) were dissolved in dry benzene (5 mL) in a test tube with a Teflon-sealed screw cap. After stirring the mixture for 15 min at room temperature, benzene (2 mL) and phosphacymantrene substrate **1** (35 μmol) were added. The test tube was sealed tightly and taken out of the glovebox. The test tube was immersed in an oil bath maintained at 23 °C and the mixture was stirred for 12 h. After quenching the reaction by addition of acetone (ca. 100 μL), the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (hexane/Et$_2$O = 5/1) to give the ARCM product as yellow-orange crystalline powder. The characterization data of the ARCM products and the condition for the chiral HPLC analysis are given below.

[η⁵-3,4-(Butan-1,4-diyl)-2-(4-diphenylphosphino-2-methylbut-2-enyl)-5-methallylphospholyl-*P*]manganese(I) Dicarbonyl (2a). Yellow solid. Mp: 197.6-197.9 °C (racemate). Yield: 19.1 mg (from 20.0 mg of **1a**, >99%; Table 1, entry 2). ^{1}H NMR ($CDCl_3$): δ 1.65-1.77 (m, 2H), 1.73 (d, *J* = 6.3 Hz, 3H), 1.83 (s, 3H), 1.93-2.03 (m, 1H), 2.05-2.14 (m, 1H), 2.39-2.55 (m, 3H), 2.64-2.78 (m, 2H), 2.89-2.94 (m, 1H), 3.03-3.14 (m, 2H), 3.19-3.33 (m, 2H), 4.78 (br, 1H), 4.82 (br, 1H), 5.05-5.10 (br m, 1H), 7.15-7.29 (m, 5H), 7.40-7.43 (m, 3H), 7.95-8.00 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.5 (s), 22.6 (s), 22.9 (d, J_{PC} = 3.2 Hz), 24.6 (s), 25.0 (s), 25.9 (dd, J_{PC} = 6.2 and 3.2 Hz), 31.2 (d, J_{PC} = 19.5 Hz), 31.6 (d, J_{PC} = 17.1 Hz), 37.4 (d, J_{PC} = 18.9 Hz), 97.2 (d, J_{PC} = 53.5 Hz), 105.8 (d, J_{PC} = 5.9 Hz), 110.4 (d, J_{PC} = 60.0 Hz), 111.6 (s), 113.0 (dd, J_{PC} = 5.0 and 2.1 Hz), 118.4 (d, J_{PC} = 5.0 Hz), 127.7 (d, J_{PC} = 9.4 Hz), 127.8 (d, J_{PC} = 8.9 Hz), 128.3 (d, J_{PC} = 2.0 Hz), 129.66 (d, J_{PC} = 7.9 Hz), 129.67 (d, J_{PC} = 2.4 Hz), 134.2 (dd, J_{PC} = 10.4 and 4.8 Hz), 138.4 (d, J_{PC} = 39.5 Hz), 140.0 (dd, J_{PC} = 9.8 and 5.3 Hz), 142.9 (d, J_{PC} = 40.9 Hz), 145.1 (s), 230.4 (d, J_{PC} = 24.5 Hz), 230.8 (d, J_{PC} = 23.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –31.3 (d, J_{PP} = 5.7 Hz), 77.9 (br). Anal. Calcd for $C_{31}H_{33}MnO_2P_2$: C, 67.15; H, 6.00. Found: C, 67.19; H, 5.96. EI-HRMS Calcd for $C_{31}H_{33}MnO_2P_2$: 554.1336. Found: 554.1326. $[\alpha]^{22}_D$ = –27.9 (*c* 1.62, $CHCl_3$ for the sample of 91% ee). Chiral HPLC Analysis Conditions: Chiralcel OD-H; eluent, hexane/^{i}PrOH = 500/1; flow rate, 0.5 mL/min; t_1 = 16.8 min, t_2 = 19.0 min.

[η⁵-3,4-(Butan-1,4-diyl)-2-(4-diphenylphosphino-2-butenyl)-5-allylphospholyl-*P*]manganese(I) Dicarbonyl (2b). Yellow solid. Mp: 200.0-200.6 °C (racemate). Yield: 12.1 mg (from 16.6 mg of **1b**, 77%; Table 1, entry 5). ^{1}H NMR ($CDCl_3$): δ 1.65-1.82 (m, 2H), 1.92-2.04 (m, 1H), 2.04-2.16 (m, 1H), 2.40-2.57 (m, 3H), 2.68-2.86 (m, 2H), 2.90-3.23 (m, 4H), 3.38-3.50 (m, 1H), 5.08-5.20 (m, 2H), 5.43-5.53 (m, 1H), 5.81-6.00 (m, 2H), 7.19-7.31 (m, 5H), 7.39-7.46 (m, 3H), 7.96-8.05 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.3 (s), 22.6 (s), 24.5 (s), 25.0 (s), 26.0 (d, J_{PC} = 19.1 Hz), 28.0 (d, J_{PC} = 15.9 Hz), 30.7 (d, J_{PC} = 17.9 Hz), 33.6 (d, J_{PC} = 17.8 Hz), 99.8 (d, J_{PC} = 47.7 Hz), 104.2 (d, J_{PC} = 5.9 Hz), 112.5 (d, J_{PC} = 59.6 Hz), 113.6 (d, J_{PC} = 3.3 Hz), 116.1 (s), 125.1 (d, J_{PC} = 4.4 Hz), 127.6 (s), 127.7 (s), 127.8 (s), 127.9 (s), 128.5 (s), 129.8 (d, J_{PC} = 8.7 Hz), 131.4 (dd, J_{PC} = 8.9 and 6.4 Hz), 133.9 (dd, J_{PC} = 10.2 and 4.4 Hz), 137.3 (d, J_{PC} = 5.4 Hz), 139.2 (d, J_{PC} = 39.0 Hz), 133.1 (s), 142.2 (d, J_{PC} = 40.9 Hz), 230.4 (d, J_{PC} = 20.2 Hz), 230.6 (d, J_{PC} = 20.2 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –32.9 (s), 77.4 (s). EI-HRMS Calcd for $C_{29}H_{30}MnO_2P_2$ (M+1): 527.1102. Found: 527.1081. Chiral HPLC Analysis Conditions: Chiralcel OD-H; eluent, hexane/^{i}PrOH = 500/1; flow rate, 0.5 mL/min; t_1 = 24.9 min, t_2 = 33.7 min.

[η⁵-3,4-(Butan-1,4-diyl)-2-(4-diphenylphosphino-2-methylbut-2-enyl)-5-prenylphospholyl-*P*]manganese(I) Dicarbonyl (2c). Yellow solid. Mp: 142.5-142.7 °C (racemate). Yield: 16.6 mg (from 18.3 mg of **1c**, >99%; Table 1, entry 6). ^{1}H NMR ($CDCl_3$): δ 1.66-1.79 (m, 2H), 1.72 (s, 3H), 1.81 (s, 3H), 1.95-2.02 (m, 1H), 2.07-2.15 (m, 1H), 2.40-2.49 (m, 2H), 2.52-2.59 (m, 1H), 2.70-2.84 (m, 2H), 2.90-2.98 (m, 2H), 3.03-3.11 (m, 1H), 3.13-3.22 (m, 1H), 3.38-3.46 (m, 1H), 5.36 (t, J = 7.6 Hz, 1H), 5.44-5.52 (m, 1H), 5.82-5.90 (m, 1H), 7.21-7.30 (m, 5H), 7.39-7.43 (m, 3H), 7.99-8.05 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.1 (s), 22.3 (s), 22.6 (s), 24.6 (s), 25.1 (s), 25.9 (s), 26.0 (d, J_{PC} = 19.8 Hz), 28.0 (d, J_{PC} = 15.9 Hz), 30.8 (d, J_{PC} = 17.9 Hz), 99.4 (d, J_{PC} = 51.7 Hz), 103.8 (d, J_{PC} = 5.9 Hz), 113.8 (d, J_{PC} = 3.3 Hz), 115.4 (d, J_{PC} = 58.7 Hz), 123.1 (d, J_{PC} = 6.5 Hz), 125.0 (d, J_{PC} = 4.4 Hz), 127.8 (d, J_{PC} = 13.9 Hz), 127.9 (d, J_{PC} = 13.2 Hz), 128.5 (s), 129.7 (s), 129.8 (d, J_{PC} = 8.3 Hz), 131.4 (dd, J_{PC} = 10.0 and 6.5 Hz), 133.1 (s), 133.85 (d, J_{PC} = 10.0 Hz), 133.94 (d, J_{PC} = 10.0 Hz), 139.4 (d, J_{PC} = 38.7 Hz), 142.3 (d, J_{PC} = 41.0 Hz), 230.51 (d, J_{PC} = 24.0 Hz), 230.55 (d, J_{PC} = 24.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –33.1 (s), 77.5 (s). $[\alpha]^{24}_D$ = –4.90 (*c* 3.10, EtOAc for the sample of 89% ee). Anal. Calcd for $C_{31}H_{33}MnO_2P_2$: C, 67.15; H, 6.00. Found: C, 67.19; H, 5.96. EI-HRMS Calcd for $C_{31}H_{34}MnO_2P_2$ (M+1): 555.1415. Found: 555.1409. Chiral HPLC Analysis Conditions: Chiralcel OD-H; eluent, hexane/^{i}PrOH = 2000/1; flow rate, 0.5 mL/min; t_1 = 45.9 min, t_2 = 50.7 min.

[η⁵-3,4-(Butan-1,4-diyl)-2-(3-diphenylphosphino-1-propenyl)-5-(2-methylpropenyl)phospholyl-*P*]manganese(I) Dicarbonyl (2d). Yellow solid. Mp: 129.3-129.5 °C (racemate). Yield: 15.9 mg (from 17.5 mg of **1d**, >99%; Table 1, entry 8). ^{1}H NMR ($CDCl_3$): δ 1.72-1.81 (m, 2H), 1.83 (s, 3H), 1.89 (s, 3H), 1.99-2.11 (m, 2H), 2.30-2.38 (m, 1H), 2.45-2.60 (m, 2H), 2.67-2.75 (m, 1H), 2.80-2.88 (m, 1H), 2.92-3.01 (m, 1H), 5.68-5.77 (m, 1H), 5.82 (d, J = 11.6 Hz, 1H), 6.29-6.33 (m, 1H), 7.27-7.31 (m, 4H), 7.34-7.40 (m, 4H), 7.67-7.72 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.6 (d, J_{PC} = 15.8 Hz), 22.67 (s), 22.74 (s), 25.3 (s), 25.5 (s), 27.2 (s), 30.4 (d, J_{PC} = 20.4 Hz), 101.6 (d, J_{PC} = 60.8 Hz), 106.0 (s), 109.6 (s), 110.9 (d, J_{PC} = 61.1 Hz), 119.8 (d, J_{PC} = 11.2 Hz), 125.6 (s), 127.1 (dd, J_{PC} = 13.8 and 13.5 Hz), 128.1 (d, J_{PC} = 8.5 Hz), 128.4 (s), 129.3 (s), 129.5 (s), 131.3 (d, J_{PC} = 8.9 Hz), 132.4 (d, J_{PC} = 8.4 Hz), 137.0 (s), 138.4 (d, J_{PC} = 38.1 Hz), 139.3 (d, J_{PC} = 41.5 Hz), 229.7 (d, J_{PC} = 19.7 Hz), 230.2 (d, J_{PC} = 24.2 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –44.4 (d, J_{PP} = 12.5 Hz), 109.4 (br). EI-HRMS Calcd for $C_{29}H_{29}MnO_2P_2$: 526.1023. Found: 526.1031. $[\alpha]^{24}_D$ = –91.3 (*c* 2.60, EtOAc for the sample of 97% ee). Chiral HPLC Analysis Conditions: Chiralpak IA; eluent, hexane/^{i}PrOH = 2000/1; flow rate, 0.5 mL/min; t_1 = 25.5 min, t_2 = 32.5 min.

[η⁵-3,4-Dimethyl-2-(3-diphenylphosphino-1-propenyl)-5-(2-methylpropenyl)phospholyl-*P*]manganese(I) Dicarbonyl (2e). Yellow solid. Mp: 115.8-116.0 °C (racemate). Yield: 17.6 mg (from 20.0 mg of **1e**, >99%; Table 1, entry 10). ^{1}H NMR ($CDCl_3$): δ 1.81 (s, 3H), 1.85 (s, 3H), 2.01 (s, 3H), 2.12 (s, 3H), 2.73-2.81 (m, 1H), 2.88-2.95 (m, 1H), 5.68-5.77 (m, 1H), 5.80 (br d, J = 8.8 Hz, 1H), 6.29-6.32 (m, 1H), 7.31-7.40 (m, 8H), 7.67-7.72 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.6 (s), 13.9 (s), 20.3 (d, J_{PC} = 12.3 Hz), 26.8 (s), 30.1 (dd, J_{PC} = 20.9 and 3.7 Hz), 103.9 (d, J_{PC} = 6.8 Hz), 105.2 (dd, J_{PC} = 59.0 and 3.0 Hz), 106.1 (d, J_{PC} = 2.5 Hz), 112.3 (d, J_{PC} = 59.7 Hz), 120.2 (d, J_{PC} = 12.9 Hz), 126.1 (d, J_{PC} = 3.7 Hz), 127.2 (dd, J_{PC} = 28.9 and 16.0 Hz), 128.16 (d, J_{PC} = 8.6 Hz), 128.20 (d, J_{PC} = 9.2 Hz), 129.4 (d, J_{PC} = 1.2 Hz), 129.5 (d, J_{PC} = 1.9 Hz), 131.6 (d, J_{PC} = 9.9 Hz), 132.3 (dd, J_{PC} = 9.8 and 1.9 Hz), 137.7 (s), 138.3 (d, J_{PC} = 38.8 Hz), 139.0 (d, J_{PC} = 40.7 Hz), 229.7 (d, J_{PC} = 19.1 Hz), 229.9 (d, J_{PC} = 19.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –47.7 (d, J_{PP} = 10.0 Hz), 106.0 (br). Anal. Calcd for $C_{27}H_{27}MnO_2P_2$: C, 64.81; H, 5.44. Found: C, 64.86; H, 5.68. HRMS Calcd for $C_{27}H_{27}MnO_2P_2$: 500.0867. Found: 500.0859. $[\alpha]^{22}_D$ = –180.5 (*c* 1.02, $CHCl_3$ for the sample of 99% ee). Chiral HPLC Analysis Conditions: Chiralpak IA; eluent, hexane/^{i}PrOH = 1000/1; flow rate, 0.5 mL/min; t_1 = 17.9 min, t_2 = 21.1 min.

Palladium-Catalyzed Asymmetric Allylic Alkylation of *rac*-1,3-Diphenyl-2-propenyl Acetate. To a mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$ (2.1 mg, 5.7 μmol), (*R*)-(–)-**2d** (6.0 mg, 11.4 μmol), KOAc (1.0 mg, 10 μmol), and *rac*-1,3-diphenyl-2-propenylacetate (40.0 mg, 159 μmol) in CH_2Cl_2 (1 mL) was added *N*,*O*-bis(trimethylsilyl)acetamide (103 mg, 506 μmol), and dimethyl malonate (67.0 mg, 507 μmol) at 0 °C under nitrogen. The flask was immersed in a bath maintained at 0 °C, and the solution was stirred for 7 days. The reaction mixture was passed through a short pad of silica gel and washed with cold CH_2Cl_2. After evaporation of the filtrate, the residue was purified by preparative TLC on silica gel (eluent: hexane/EtOAc = 5/1) to give the alkylated product of (*S*)-configuration in pure form. Yield: 28.1 mg (86.6 μmol, 54%). The enantiopurity and the absolute configuration of the product were determined as reported.[25]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: *********.

NMR spectra (^{1}H, ^{13}C and ^{31}P) and chiral HPLC chromatograms for all the new compounds (PDF)

Crystallographic data for (*R*)-(–)-**2d** (CIF)

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Notes

The authors declare no competing financial interest.

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